

Precision hydrogen trace gas detection by ultralow-loss multipass cavity Raman scattering

Jaspreet Singh and Andreas Muller

Department of Physics, University of South Florida, 4202 E Fowler Ave, Tampa, FL 33620, USA.

Email: mullera@usf.edu

Abstract: Raman scattering with a feedback-assisted ultralow-loss multipass cavity was implemented for trace hydrogen sensing. A limit of detection (precision) of 40 (50) parts-per-billion was obtained at a pressure of 0.2 MPa in a 30-min exposure. © 2023 The Author(s)

Hydrogen (H_2) is anticipated to play a major role in energy storage and power generation, e.g., in fuel cells, potentially aiding decarbonization and sustainable development. Concomitantly, accurate trace sensors are needed, for instance for monitoring inadvertent hydrogen losses. Due to its low ambient concentration of 0.55 parts-per-million (ppm), hydrogen also has potential as a replacement for expensive helium-based leak detectors. In medical diagnostics, precision hydrogen measurements are at the heart of the “hydrogen breath test”.

Despite its simple makeup, however, hydrogen gas remains difficult to detect at concentrations of few parts-per-million (ppm) and below. Established optical methods such as cavity ring-down spectroscopy (CRDS), off-axis integrated cavity output spectroscopy (ICOS), and quantum cascade tunable infrared laser differential absorption spectroscopy (QC-TILDAS) are largely ineffective, since only quadrupole H_2 transitions are infrared allowed [1]. Gas chromatography or magnetic resonance-based methods, although trace-sensitive, are generally bulky, expensive, and not readily portable. Consequently, the most widely adopted H_2 detection methods today use micro-electromechanical systems (MEMS) or metal oxide semiconductor (MOS) devices. The advantages of these devices include high speed, extreme miniaturization, and low cost [2]. However, poor chemical specificity and the need for recurrent calibration effectively makes accurate H_2 detection at concentrations of order 100 parts-per-billion (ppb) a formidable challenge.

An attractive alternative is offered by spontaneous Raman scattering (SRS). SRS stands out as an economical and robust technique that elicits a unique spectral signature from any molecular gas, and, depending on resolution, can detect dozens of analytes simultaneously, including isotopologues. Recently, numerous SRS enhancement techniques using capillaries, hollow core photonic crystal waveguides, or optical cavities have improved the prospects of SRS trace sensing applications, many demonstrating detection limits nearing the 10 ppm range.

A particularly simple enhancement approach consists in combining a multimode laser diode with a near-concentric retro-reflecting multipass cavity using spectrally-sensitive feedback. This effective external cavity diode laser features narrowed linewidth (3.5 cm^{-1}) and high circulating power (80 W), and was shown to provide SRS rates high enough to detect ambient hydrogen, albeit with high noise [3].

We report here a significantly improved implementation of feedback-assisted multipass SRS with the use of ultralow-loss mirrors. A thorough noise analysis reveals that, after eliminating direct sources of background, e.g.,

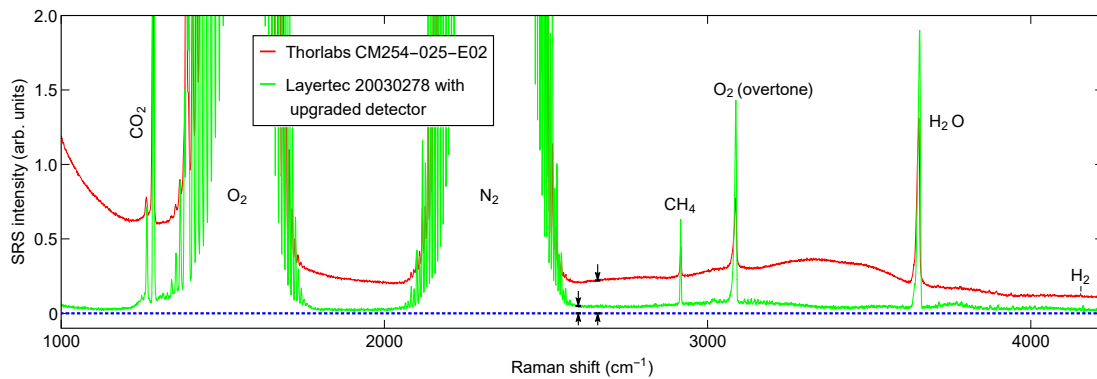


Fig. 1: Raman spectra of dried room air (exposure time was 60 seconds and the pressure was 0.1 MPa) using commercial off-the-shelf mirrors (red, Thorlabs CM254-025-E02), and ultralow-loss mirrors (Layertec) also with an upgraded detector (green), with arrows indicating the midrange background magnitude.

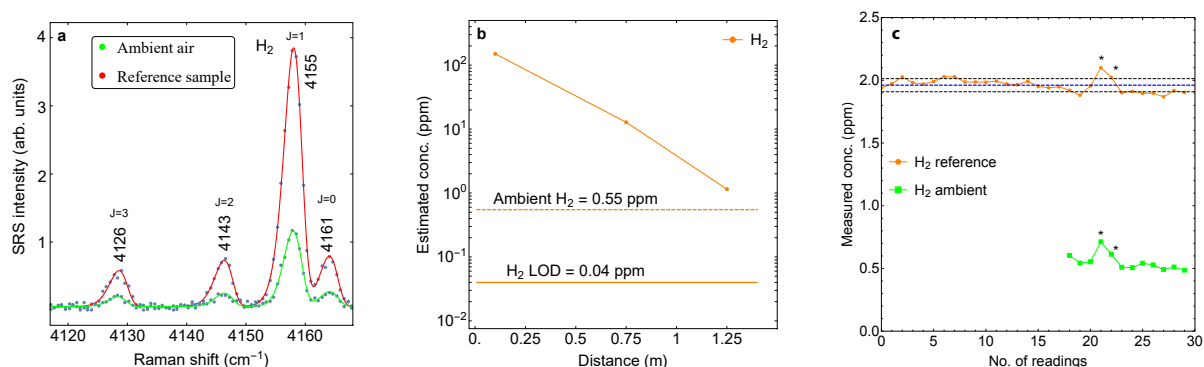


Fig. 2: (a) Rovibrational SRS spectra of dried ambient air (in green, 0.55 ppm hydrogen concentration) and a reference 1.961 ppm certified hydrogen gas sample (in red), cumulative 15 exposures of 120 s duration each at 0.2 MPa absolute pressure. (b) Logarithmic plot of H_2 concentration in car exhaust air measured at various distances to the idling vehicle. (c) Outcome of repeated measurements reveals a root means square precision of 50 ppb. Outliers (*) are associated with optical misalignment identified after recording.

with adequate spectral filters, the dominant source of noise remaining is due to background light generation in the multipass mirrors themselves. These mirror scattering losses further limit the overall achievable reflectivity, and thus the overall enhancement of the cavity.

A cavity based on custom ion-beam sputtered ultralow-loss mirrors (>99.995% reflectivity from 440–550 nm, Layertec) was constructed and characterized. In comparison to off-the-shelf commercial mirrors, several spectroscopic improvements were obtained, including: (i) an average reduction of background intensity by a factor of 10, and (ii) an average increase of SRS intensity by a factor of 5, leading to an overall increase in average signal-to-background ratio by a factor of 30 (Fig. 1). Hydrogen rovibrational spectra (pump wavelength of 443 nm) were recorded for various ambient air samples, and for a 1.961 ppm certified reference sample (Airgas), as shown in Fig. 2(a). In order to optimally extract the H_2 concentration and its uncertainty, a least squares fitting of the first four rotationally-resolved transitions ($J=0,1,2,3$) was implemented with four slightly asymmetric gaussian lineshapes. The fitted parameters provide an accurate measure of the curve area, A_{H_2} , which is proportional to the H_2 number density. To correct for unavoidable fluctuations associated with optical alignment, chamber pressure, laser power, etc., A_{H_2} was normalized by A_{O_2} , the area of the oxygen overtone transition at 3088 cm^{-1} . We estimate the limit of detection—defined here as the concentration at which the signal to noise ratio is 5—as 40 ppb for a 30-min long measurement.

Figure 2(b) illustrates the resultant H_2 sensitivity in a real world example, namely the analysis of gasoline engine exhaust gas. The H_2 concentration is seen to rapidly diminish as air is sampled farther away from the car exhaust outlet, and even at a distance of over 1 m it is possible to differentiate it from the average ambient concentration. Repeated measurements of the reference sample H_2 concentration further allow the estimation of uncertainty. As seen in Fig. 2(c), although variations from the mean do occur, the root mean square deviation, a measure of precision, is only 50 ppb in a sample series spanning over a week.

In summary, ultralow-loss mirrors were found to be an enabling component for achieving high precision trace detection with multipass SRS. Our measurements reveal nearly shot noise limited detection with all elements of the setup, including the detector itself, operating at room temperature.

Acknowledgement: The authors acknowledge the financial support from the National Science Foundation (NSF grant No. 2116275).

References

1. V. Avetisov, O. Bjoroey, J. Wang, P. Geiser, and K. G. Paulsen, “Hydrogen sensor based on tunable diode laser absorption spectroscopy,” *Sensors* **19**, 5313 (2019).
2. P. S. Chauhan and S. Bhattacharya, “Hydrogen gas sensing methods, materials, and approach to achieve parts per billion level detection: A review,” *Int. journal hydrogen energy* **44**, 26076–26099 (2019).
3. J. S. G. Velez and A. Muller, “Spontaneous raman scattering at trace gas concentrations with a pressurized external multipass cavity,” *Meas. Sci. Technol.* **32**, 045501 (2021).